Applied Catalysis B: Environmental 217 (2017) 581–590

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Influence of hydrocarbon species on its adsorption on a VSCR catalyst under simulated diesel engine operating conditions

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ARTICLE INFO

Article history:
Received 2 February 2017
Received in revised form 20 May 2017
Accepted 26 May 2017
Available online 3 June 2017

Keywords:
Vanadia SCR
Hydrocarbon adsorption
Temperature programmed oxidation
Dodecane
Toluene
Squalane

ABSTRACT

Vanadia-SCR (VSCR) is a proven technology for reducing diesel engine NO_x emissions using urea hydrolysis derived NH_3 as a reductant. It is also known that VSCR is active for hydrocarbon (HC) oxidation. However, HC species from diesel engine exhaust may be adsorbed onto VSCR at low exhaust temperatures such as under low engine load or idle conditions. The adsorbed HC may be gradually transformed into more stable coke during engine operation. The accumulated HC or coke on VSCR can result in decreased NO_x conversion efficiency due to blockage of catalyst pores and active sites. In addition, rapid oxidation of accumulated HC or coke can lead to exotherms which can thermally damage the VSCR and may lead to vanadium and tungsten release. This work investigates the fundamental adsorption characteristics of HC species on a state-of-the-art VSCR catalyst in the low temperature region. Dodecane and toluene are used as model molecules for alkane and aromatic species from unburned diesel fuel, while squalane is used as a model molecule for unburned lube oil.

1. Introduction

NO_x (NO and NO_2), HC (hydrocarbon) and PM (particulate matter) are all emitted from diesel engines. The substantial reduction of these pollutants has been driven by more and more stringent regulations and enabled by new diesel engine, aftertreatment system, fuel and lube oil technologies [1,2]. Vanadia-based and metal promoted zeolite-based SCR catalysts are proven technologies for NO_x reduction. Because of VSCR's high NO_x conversion efficiency, low cost, excellent durability and chemical resistance to sulfur poisoning, VSCR catalysts are widely used for NO_x reduction in diesel exhaust aftertreatment systems, especially in Euro IV, Euro V and off-road applications. In these applications, VSCR catalysts are directly exposed to engine exhaust, and DEF (diesel exhaust fluid with 32.5 wt.% urea in aqueous solution) is injected upstream of the VSCR, producing the NH_3 required to reduce NO_x via the well documented SCR reactions. A significant amount of fundamental research has been conducted over the past several decades to understand the SCR reaction mechanism over VSCR catalysts in order to improve catalyst reactivity, stability and elucidate catalyst deactivation mechanisms from various poisons [3–7]. It was previously reported that VSCR catalysts can contribute to HC and PM reduction as well [8–11].

Diesel engine exhaust is a complex mixture. N_2, H_2O, CO_2 and O_2 are the main constituents resulting from lean combustion of diesel fuel. If complete combustion of fuel is assumed, the H_2O, CO_2 and O_2 concentration can be calculated as a function of air/fuel mass ratio as illustrated in Fig. 1. Increasing air/fuel mass ratio increases O_2 concentration, while the H_2O and CO_2 concentrations decrease. Diesel engines are typically operated with an air/fuel mass ratio from 20 to 30; therefore, 5–10% O_2 and 6–9% H_2O/CO_2 are typically observed in diesel engine exhaust. Under idle conditions, the air/fuel mass ratio may exceed 160 due to decreased fuel injection. Thus, significantly lower H_2O concentration (<2%) and much higher O_2 concentration (>18%) can be expected.

Engine out HCs resulting from diesel combustion can be attributed to unburned and/or partially-burned diesel fuel and lube oil. Total HC concentration, typically from tens to a few hundred ppm of C1 (methane equivalent), and composition highly depend on engine characteristics, fuel and lube oil properties, engine operating conditions, exhaust sampling and measurement techniques. Many studies have been carried out to speciate light and semi-volatile HCs from diesel combustion in order to optimize combustion processes and reduce emissions [12–18]. Light HCs (C12 and below), typically unsaturated, including alkenes and alkynes commonly sampled by Tedlar bag, are primarily from partially combusted products; while semi-volatile HCs, commonly sampled by resin trap, are generally considered from unburned diesel fuel [14,17,18]. For example, Hammerle et al. studied HC emissions from a diesel-fueled vehicle using a dilution tunnel, and

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http://dx.doi.org/10.1016/j.apcatb.2017.05.077
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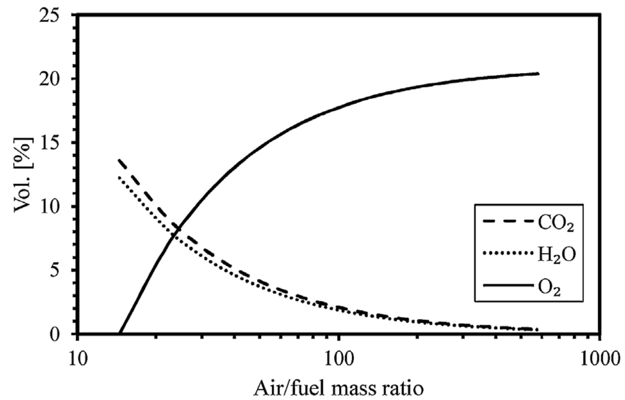


Fig. 1. Lean burn diesel engine emissions of CO_2, H_2O and O_2 volumetric concentration as a function of air/fuel mass ratio greater than the stoichiometric ratio of 14.5. Diesel fuel was assumed to be completely combusted to CO_2 and H_2O.

they reported total HC emissions of 91 mg/Km as measured by hot FID (flame ionization detector). Light HC (C12 and below) and semi-volatile HC accounted for 45% and 9% of the total HC, respectively [16]. In contrast, Han et al. conducted diesel engine exhaust HC speciation without dilution and they found that HC emissions from a conventional diesel engine are composed of 46% partially oxidized and 54% unburned diesel fuel [13]. In addition to light HCs and unburned diesel fuel, oxygenated organic species such as aldehydes, ketones and carboxylic acids etc. are also reported [2,14,19].

Lube oil is used in diesel engines to reduce the friction created by moving parts, such as pistons, valve stems, the turbo shaft etc., and increase the performance of the diesel engine. Lube oil consumption highly depends on engine operating conditions. As an approximation, the lube oil consumption rate is about 0.1% of diesel fuel consumption [20]. Because lube oil consists of relatively stable, high molecular weight HCs from approximately C14–C45 [21], and it is applied to the surfaces of moving parts, such as piston rings, where the temperature is significantly lower than combustion temperature, a significant portion of lube oil can survive combustion. Miller reported that 30–80%, with an average of 64%, of oil consumed can survive combustion and contribute to soluble organic fraction (SOF) formation on PM, and that the amount of oil derived SOF trends approximately linearly with oil consumption [20]. Lube oil derived HC can exist in the gas phase in the combustion chamber or in piping close to the engine where the exhaust temperature is high. As exhaust temperature decreases, due to the heat loss in the exhaust piping, aftertreatment system or exhaust sampling apparatus, the oil derived HC condenses onto soot particles, forming SOF. Thus, the SOF contributes to a significant portion of engine out PM [22]. Although both unburned diesel fuel, especially the high molecular weight fraction, and lube oil are both considered to contribute significantly to the SOF fraction of PM [2,22–24], many SOF chromatography analysis results indicate that the eluted SOF contents most closely resemble lube oil [15,24–26]. Sakurai et al. applied a thermal desorption particle beam mass spectrometer (TDPBMS) and tandem differential mobility analyzer (TDMA) to conduct on-line measurement of the chemical composition and volatility of diesel exhaust particles from a modern, heavy-duty diesel engine under various load conditions. The authors found that the organic components of diesel particles are almost entirely (95%) derived from unburned lube oil [15].

Gas phase HCs are known to inhibit NO_x conversion over VSCR catalysts [8,9]. The presence of gas phase HC, such as propylene, can also lead to lowered NO_x conversion in the mid and/or high temperature range due to excess NH_3 consumption via ammoxidation [27]. In addition, HC can adsorb and accumulate on vanadia-based catalysts and lead to catalyst deactivation. For example, Ottinger et al. observed carbonaceous materials accumulated on a field returned VSCR catalyst from a diesel aftertreatment system and found the NO_x conversion was significantly diminished on the as-received catalyst below 300 °C. Thermal treatment at 500 °C with the presence of O_2 can remove the carbonaceous deposit by oxidation and fully recover the catalyst performance [8]. In addition to the negative impact on NO_x conversion from accumulated carbonaceous materials, rapid oxidation of the accumulated HC or coke can lead to exotherms on the catalyst which can thermally damage the VSCR catalyst if the temperature exceeds 550 °C [28] and can lead to vanadium and tungsten release [29].

This work focuses on understanding the effect of different types of HC species on their adsorption on a state-of-the-art VSCR catalyst in the low temperature region under relevant diesel engine operating conditions. Dodecane and toluene are used as model molecules for alkane and aromatic species from unburned diesel fuel. Squalane, due to its physical and chemical similarities to lube oil, is chosen as a model molecule for unburned lube oil [30]. The effects of O_2 and H_2O are discussed in the context of engine operating conditions to elucidate the HC adsorption mechanisms and its chemical transformation behaviors.

2. Experimental

2.1. Catalyst sample

The micro-core catalyst samples were cut from the inlet face of a fresh, washcoated, state-of-the-art $V_2O_5/WO_3/TiO_2$ (VSCR) catalyst element with 300 CPSI (cells per square inch). The catalyst sample has ~6.4 mm (1/4 inch) diameter and 25.4 mm (1 inch) length containing 12 intact channels. The total mass of the micro-core sample is 0.48 g.

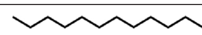
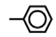
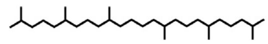
2.2. Flow reactor system

A flow through reactor was used to conduct the HC adsorption and temperature-programmed oxidation (TPO) experiments to characterize and quantify the adsorbed HC on the VSCR catalyst. The configuration of the reactor system has been reported in several previous publications [6,28,31]. Briefly, the reactor utilizes 14 MKS mass flow controllers (MFCs) for metering and monitoring reaction gas flow rate. The reaction gases, Ar, O_2, 400 ppm (parts per million by volume) toluene/Ar are supplied by AirGas in cylinders and are all UHP grade or higher. Water vapor in the reaction gas mixture is generated by feeding deionized water into a Bronkhorst liquid mass flow controller and evaporator system. Liquid HC, such as dodecane and squalane/dodecane mixture, was introduced to the reaction gas mixture with a second Bronkhorst liquid mass flow controller and evaporator system. The quartz reactor tube is 22 inches long with 7 and 9.5 mm for inner and outer diameters, respectively. The reactor tube is horizontally placed in a Lindberg Blue M miniMite tube furnace for temperature control. Type K thermocouples (0.02 inch diameter) are instrumented at both inlet and outlet of the catalyst bed for temperature control and measurement. The composition of the reaction gas mixture, either after passing through the catalyst bed or the reactor by-pass line, is analyzed by a MKS 2030 Fourier transform infrared (FTIR) spectrometer. All the gas lines are constructed using Swagelok stainless steel tubing and fittings, and they are heated to ~200 °C to avoid condensation and adsorption of H_2O and HC species.

2.3. HC adsorption experiments

To simulate the typical lean-burn diesel engine exhaust gas composition, 8 vol.% H_2O and 10 vol.% O_2 in balance Ar were used as baseline gas unless otherwise indicated. CO_2 was not included in

Table 1
Properties of HCs.

HC	Formula	Molecular structure	Molecular weight [g/mol]	Boiling point [°C]
Dodecane	$C_{12}H_{26}$		170.3	216
Toluene	C_7H_8		92.1	111
Squalane	$C_{30}H_{62}$		422.8	350

the baseline gas in this study because ppm levels of CO_2 must be measured during TPO experiments to quantify the carbonaceous material stored during HC adsorption. All the flow reactor experiments were conducted at 60 k h^{-1} GHSV (gas hourly space velocity) by flowing 804 sccm (standard cubic centimeters per minute) total gas mixture at ambient pressure. The fresh VSCR catalyst sample was first degreened (DG) at 525 °C for 2 h under baseline gas in the flow reactor to stabilize the catalyst. For HC adsorption experiments, unless otherwise indicated, a constant total HC concentration of approximately 1000 ppm C1 was maintained. Therefore, for toluene adsorption experiments, ~140 ppm toluene was introduced; for dodecane adsorption experiments, ~90 ppm dodecane was introduced. The exhaust concentration of lube oil derived HC is estimated to be approximately 50 ppm C1 by assuming an air/fuel mass ratio of 25, a 0.1% oil consumption rate relative to fuel consumption and 64% [20] lube oil survival rate. Because squalane has a high boiling point of 350 °C and to facilitate its introduction to the reaction gas mixture via the Bronkhorst liquid mass flow controller, a solution of squalane and dodecane was prepared with 5 wt.% of squalane. Therefore, with a total of 1000 ppm C1 HC feeding, there is approximately 1.7 ppm squalane and approximately 85 ppm dodecane in the gas mixture. For simplicity, this condition will be referred to as squalane adsorption. In general, HC adsorption and TPO experiments are conducted in three steps:

- Catalyst cleaning: either via DG for a fresh catalyst sample or at 500 °C for 30 min under baseline gas for a previously degreened catalyst.
- HC adsorption: cool the catalyst to the target HC adsorption temperature under baseline gas, unless otherwise indicated. Then, introduce HC at the desired concentration for 2–12 h.
- TPO: stop introducing HC but continue to flow baseline gas at the HC adsorption temperature for 1 min to flush the residual HC in the reactor system. Then, ramp the catalyst temperature at 10 °C/min to 500 °C.

To study the effect of O_2 and H_2O concentration on HC adsorption, the baseline gas composition was modified during the 2nd step of HC adsorption.

2.4. Material characterization

Dinitrogen (N_2) adsorption experiments were conducted at −196 °C to obtain the BET (Brunauer-Emmett-Teller) surface area using a Micrometrics TriStar II 3020 physisorption analyzer. The DG micro-core catalyst was first degassed under vacuum at 350 °C for 2 h; while the HC adsorbed catalyst samples were degassed at 80 °C for 1 h under flowing N_2 to avoid decomposition/vaporization of adsorbed HC species. Diffuse reflectance Fourier transform infrared spectra (DRIFTS) were collected at room temperature with a Nicolet 6700 spectrometer with a Harrick Praying Mantis diffuse reflectance accessory using a liquid N_2 cooled MCT detector. HC loaded catalyst samples were prepared ex-situ in the micro-core reactor described above. The HC adsorbed catalyst was then unloaded from the quartz reactor tube and crushed into powder

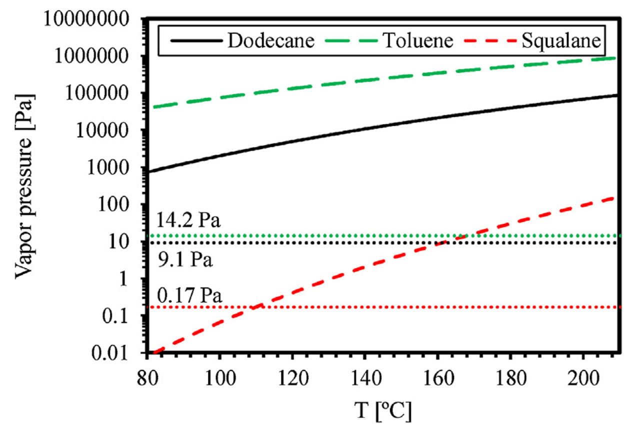


Fig. 2. Vapor pressure of pure substances as a function of temperature for dodecane, toluene and squalane based on Antoine equation.

before infrared spectra were taken at room temperature. The spectra were averaged from 32 scans at a resolution of 4 cm^{-1}. All spectra are background corrected.

3. Results

3.1. Properties of HC adsorbates

Three different types of HCs—dodecane, toluene and squalane—were used for studying HC adsorption on VSCR in the low temperature range. Dodecane and toluene are chosen as model molecules for alkanes and aromatics from unburned diesel fuel, and squalane, a heavy HC, is chosen as a model molecule for lube oil. The molecular structure, chemical formula and boiling point for the three HCs are listed in Table 1. Squalane, containing thirty carbon atoms, is a much heavier HC than dodecane or toluene, and it also has a much higher boiling point. The vapor pressure of the HCs is calculated based on the Antoine equation [32,33], and the results are shown in Fig. 2. Under ambient conditions, all three of these HCs are liquids. Toluene, due to its low molecular weight, has the highest vapor pressure, increasing from ~3.9×10^4 Pa at 80 °C to ~7.5×10^5 Pa at 200 °C. Squalane, due to its higher molecular weight, has several orders of magnitude lower vapor pressure than toluene and dodecane from 80 to 200 °C. For dodecane and toluene adsorption experiments on VSCR, 1000 ppm C1 concentration is typically used in this work, which corresponds to 9.1 Pa (~90 ppm) for dodecane and 14.2 Pa (~140 ppm) for toluene at ambient pressure. As shown in Fig. 2, the inlet concentrations of dodecane and toluene are two to three orders of magnitude lower than their corresponding saturation vapor pressures from 80 to 200 °C. Therefore, condensation of dodecane and toluene under the conditions evaluated in this work can be excluded. On the other hand, as illustrated in Fig. 2, below 110 °C, 0.17 Pa of squalane (50 ppm C1) is greater than squalane's saturation vapor pressure. Thus, thermodynamically, below 110 °C, 50 ppm C1 of squalane could condense.

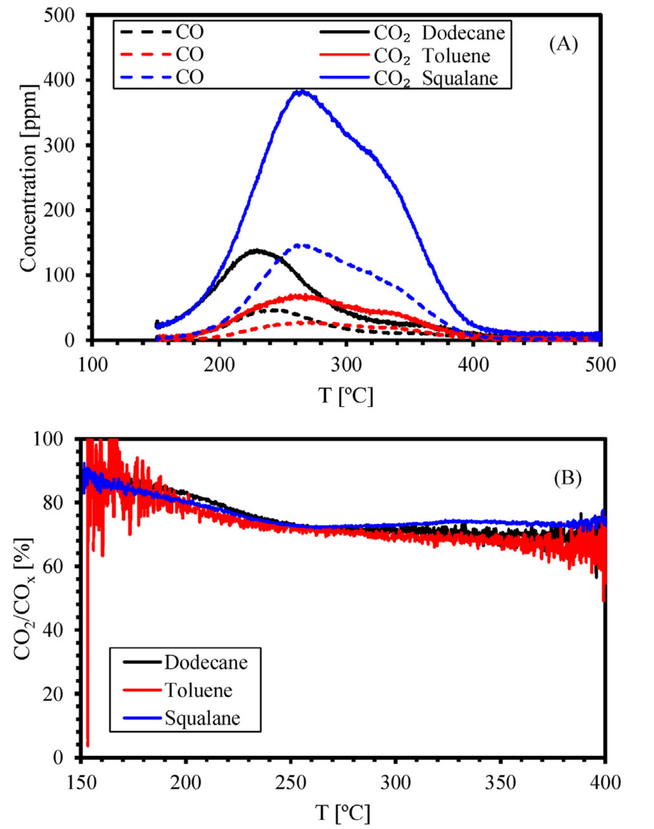


Fig. 3. (A) CO, CO_2 release profile during temperature-programmed oxidation (TPO) after dodecane, toluene and squalane adsorption at 150 °C for ~6 h; (B) CO_2/CO_x ratio during the TPO after dodecane, toluene and squalane adsorption at 150 °C for ~6 h.

3.2. HC adsorption

HC adsorption experiments, using dodecane, toluene and squalane as adsorbates, were conducted over the cleaned VSCR catalyst. The adsorbed carbonaceous material was characterized using the TPO technique. The representative TPO CO and CO_2 release profiles and CO_2/CO_x ratio after dodecane (1000 ppm C1), toluene (1000 ppm C1) and squalane (50 ppm C1 with 950 ppm C1 from dodecane) adsorption at 150 °C for ~6 h are illustrated in Fig. 3A and B, respectively. The CO and CO_2 release during the TPO following dodecane adsorption in Fig. 3A have similar profiles, but the CO_2 signal is 3–4 times higher than CO. Both CO and CO_2 start to evolve at 150 °C and have a major low temperature peak at ~230 °C and a broad, smaller high temperature shoulder from 300 to 400 °C. The TPO after toluene adsorption displays a similar pattern to the TPO following dodecane adsorption, except that the low temperature CO and CO_2 peak at ~260 °C is much smaller than the corresponding low temperature dodecane peak. The high temperature toluene peak is slightly larger than that from dodecane adsorption. For squalane adsorption, only 1.7 ppm squalane (50 ppm C1) together with ~85 ppm dodecane were introduced. However, the CO and CO_2 release profiles after squalane adsorption display much stronger signals than dodecane and toluene adsorption, indicating that a much higher amount of HC was adsorbed at the same adsorption temperature and duration. Fig. 3B shows the CO_2/CO_x ratios during the TPO experiments. Regardless of the significant differences in the three HCs, the resultant CO_2/CO_x ratios are quite similar and did not vary significantly as a function of temperature. The CO_2/CO_x ratio decreases from nearly 90% at 150 °C to ~72% at 250 °C and then slowly decreases to ~68% at 400 °C. Since the CO_2/CO_x profile as a function of temperature is only minimally affected by different adsorption conditions, such as adsorption temperature, duration and base gas environment, only the total CO_x profile will be reported henceforth.

A series of HC adsorption experiments were conducted using the three HC adsorbates at different temperatures and for various durations under the baseline gas environment. The CO_x release profiles and the carbon loading, calculated by integrating under the CO_x release profiles during the TPO are shown in Fig. 4.

Fig. 4A displays the carbon loading after dodecane adsorption at various temperatures and durations and Fig. 4a displays the TPO CO_x release profile after 150 °C dodecane adsorption for various durations. In general, the carbon loading as a result of dodecane adsorption at constant temperature slightly increases with adsorption duration from ~2 h to ~12 h. Carbon loading at 80 °C is approximately 15–20 mmol/L. Increasing the adsorption temperature to 125 °C, carbon loading increases to 80–100 mmol/L. Carbon loading starts decreasing as the adsorption temperature increases above 125 °C. The TPO CO_x release profiles after dodecane adsorption at 150 °C are shown in Fig. 4a. With increasing adsorption duration from 3 to 13 h, the TPO CO_x profile does not vary significantly. Through peak deconvolution, the peak temperatures and peak area were obtained. A set of representative peak deconvolution results are shown in Fig. 4a for dodecane adsorption at 150 °C for 13 h. The peak temperatures and the high temperature peak area percentage are listed in Table 2. As shown in Table 2, the CO_x low temperature peak increases from ~205 °C to ~240 °C when the adsorption temperature increases from 80 °C to 175 °C. However, the CO_x high temperature peak remains relatively constant at ~340 °C, independent of adsorption temperature and duration. With increasing dodecane adsorption temperature, the high temperature CO_x peak area fraction increases from 8% to 20%.

Carbon loading and representative TPO CO_x release profiles after constant temperature toluene adsorption are shown in Fig. 4B and Fig. 4b, respectively. In general, carbon loading from toluene adsorption behaves similarly to that of dodecane. The carbon loading from toluene adsorption at 80 °C is negligible (data not shown). With increasing adsorption temperature from 100 °C to 200 °C, carbon loading increases from ~15 mmol/L to ~90 mmol/L after the 2–12 h adsorption. Above 200 °C, the carbon loading decreases as shown in Fig. 4B, likely due to the increased oxidation rate of adsorbed HC at higher temperature. The carbon loading from toluene adsorption (Fig. 4B) is quite stable after 2 h of adsorption at the low temperatures evaluated, similar to dodecane adsorption. To better understand the initial toluene adsorption process, experiments were conducted with durations from 0.1 h to 2 h at 200 °C, and the results are presented in Fig. 4B. It appears that the carbon loading increases substantially within the first half hour, and then the rate of adsorption slows. The catalyst is saturated after the 2 h adsorption at 200 °C. The TPO CO_x profiles after toluene adsorption at 150 °C are shown in Fig. 4b. Carbon loading slightly increases with increasing toluene adsorption duration at 150 °C as can be seen from the increase in CO_x signals in Fig. 4b. However, the overall peak profile remains similar. The peak deconvolution results are shown in Fig. 4b for the 11 h toluene adsorption at 150 °C, and the detailed results are listed in Table 2. The low temperature CO_x peak shifts from ~220 °C to ~280 °C as the toluene adsorption temperature increases from 100 °C to 200 °C. The high temperature CO_x peak slightly shifts ~20 °C toward higher temperature. Unlike TPO results from dodecane adsorption, the high temperature CO_x peak fraction decreases approximately 10 ~ 15% as adsorption temperature increases from 150 °C to 200 °C.

Fig. 4C and Fig. 4c presents the squalane adsorption results. As previously discussed in Section 2.3, a squalane concentration of 50 ppm C1 was selected to approximate the engine out exhaust concentration of lube oil derived HC. Squalane adsorption at 80 and 100 °C display a similar amount of carbon loading, which is 25–35% higher than the loading after 150 °C adsorption. In con-

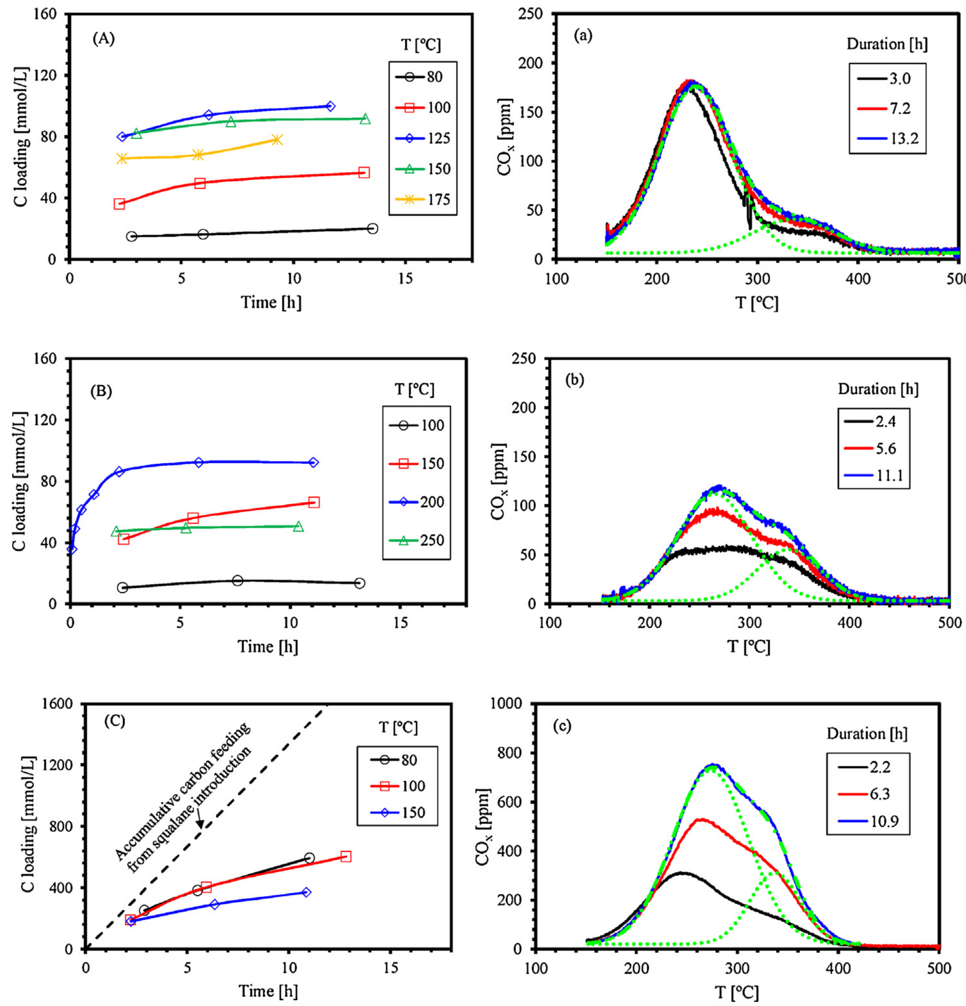


Fig. 4. Carbon loading as a function of adsorption temperature and adsorption time for (A) dodecane; (B) toluene; (C) squalane. TPO CO_x release profile after adsorption at 150 °C for (a) dodecane; (b) toluene; (c) squalane. Each TPO CO_x release profile is fitted with two normal distribution curves. Representative peak deconvolution results are shown for the blue curves in (a), (b) and (c). The two dotted green curves are the fitted low and high temperature peaks and the dash-dotted green curve is the overall fitting. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

trast to dodecane and toluene adsorption, carbon loading from squalane adsorption is significantly higher at the same adsorption temperature and similar duration. In comparison to the dodecane adsorption results shown in Fig. 4A, it can be concluded that the substantial increase in carbon loading results from the addition of 1.7 ppm squalane to the HC feed. In addition, carbon loading continues to increase with increasing squalane adsorption duration, and the VSCR does not appear to be saturated even after ~12 h. The total carbon exposure from introducing ~1.7 ppm squalane is calculated and plotted in Fig. 4C as a dash line. Comparing the carbon loading from squalane adsorption, it is clear that a significant portion (30–60%) of squalane is adsorbed onto the VSCR catalyst. Fig. 4c shows the TPO results after squalane adsorption at 150 °C. The CO_x signal is significantly higher than that from dodecane and toluene adsorption due to the much higher carbon loading from squalane adsorption. In addition, as can be seen in Fig. 4c and Table 2, the low temperature CO_x peak displays an increase of 30–40 °C with prolonged adsorption duration. In contrast, the increase in the low temperature peak is within 10 °C in the case of dodecane and toluene. Relatively, the high temperature CO_x peak is more stable, at approximately 335 °C, regardless of squalane adsorption temperature and duration.

3.3. Effect of temperature cycling

Engine exhaust temperature could vary in a wide range due to the constant change in engine speed and torque under transient operation. To study the effect of the exhaust temperature variation on HC adsorption, the following experiment was designed and conducted on the cleaned VSCR catalyst. 1) perform squalane adsorption at 100 °C for ~2 h under baseline gas; 2) ramp the temperature to 225 °C at 5 °C/min and hold at 225 °C for 30 min while maintaining the same adsorption gas environment; 3) then reduce the temperature to 100 °C under the same gas environment; 4) repeat steps 1 through 3 four more times; 5) reduce the temperature to 100 °C under baseline gas and conduct a TPO by ramping the temperature to 500 °C at 10 °C/min. The final TPO results are shown in Fig. 5. There is a main high temperature peak at 342 °C and a broad low temperature shoulder near 300 °C. In comparison to the TPO results after squalane constant temperature adsorption at 100 °C for 13 h, as plotted in Fig. 5, the majority of the strong low temperature CO_x peak at 262 °C is removed and becomes a broad, low intensity shoulder. The high temperature CO_x peak size is partially decreased with the peak temperature increased more than 30 °C.

Table 2
TPO CO_x deconvolution results.

Adsorbate	Adsorption T [°C]	Duration [h]	CO_x low T peak [°C]	CO_x high T peak [°C]	High T CO_x peak fraction [%]
Dodecane	100	2.2	203	345	8
		5.8	207	347	8
		13.2	214	355	8
	125	2.3	212	334	9
		6.2	223	343	9
		11.7	228	344	10
	150	3.0	230	338	14
		7.2	235	340	16
		13.2	238	336	19
	175	2.3	236	343	17
		5.7	241	341	21
		9.3	240	340	20
Toluene	100	2.4	229	331	–
		7.6	229	331	–
		13.2	213	320	–
	150	2.4	254	335	32
		5.6	259	336	32
		11.1	265	339	29
	200	2.2	275	353	18
		5.9	284	356	16
		11.1	285	354	18
Squalane	80	2.9	233	334	16
		5.5	247	337	16
		11.0	261	335	24
	100	2.2	224	327	18
		5.9	248	332	20
		12.8	262	329	32
	150	2.2	246	333	22
		6.3	265	337	26
		10.9	273	337	21

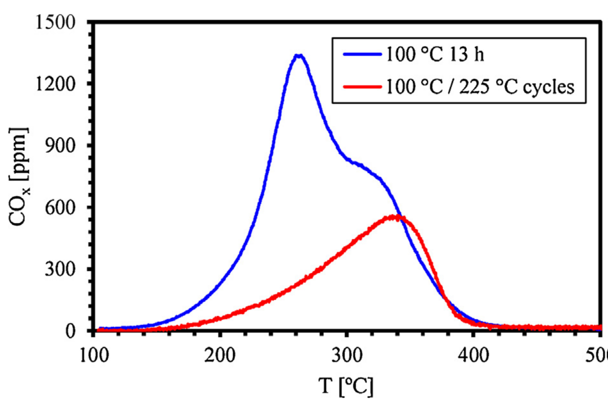


Fig. 5. TPO CO_x release profile after squalane adsorption at 100 °C for 13 h and squalane adsorption after five cycles of 100 °C for 2 h and 225 °C for 0.5 h.

3.4. Effect of H_2O and O_2

In general, diesel engines are always operated under lean conditions. The air-fuel mass ratio under normal operation is around 20–30; therefore, the engine exhaust would contain 5–10 vol.% H_2O and O_2 as shown in Fig. 1. However, under engine idle conditions, the air-fuel mass ratio can exceed 160, and as a result the engine exhaust H_2O content will decrease to below 2 vol.%. Correspondingly, the O_2 concentration will be above 19 vol.%, close to the O_2 level in ambient air. It is worth mentioning that when operating at idle conditions, the engine exhaust temperature is low. Therefore, the temperature of the downstream VSCR catalyst will be approximately 80–150 °C, mainly depending on the environmental temperature. The carbon loadings from HC adsorption experiments performed with the baseline gas environment and under the simulated idle gas environment with 19% O_2 and 1.5% H_2O are compared in Fig. 6A. Experiments are conducted at 150 °C for ~2 h. Results for each HC species are normalized to the carbon loading measured

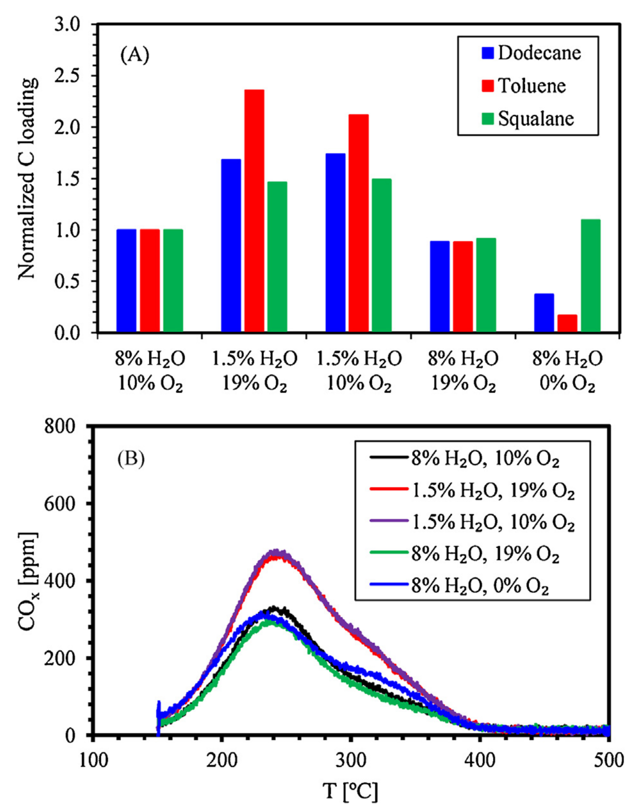


Fig. 6. (A) Normalized carbon loading under different adsorption gas environments at 150 °C for ~2 h for dodecane, toluene and squalane; (B) TPO CO_x release profile after squalane adsorption at 150 °C under various gas environments.

under the baseline gas environment. As can be seen in Fig. 6A, the carbon loading of all three HC species increases under simulated idle gas conditions. Dodecane, toluene and squalane adsorption

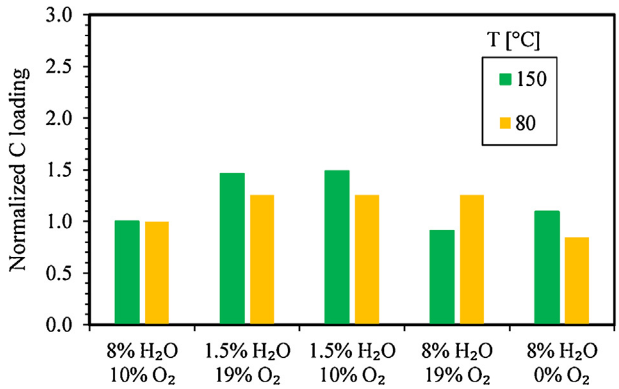


Fig. 7. Normalized carbon loading after squalane adsorption at 150 °C and 80 °C for ~2 h under different adsorption gas environments.

increased 68%, 136% and 46%, respectively. To understand the cause of the observed increase in carbon loading under engine idle gas environment relative to the baseline gas, controlled experiments were performed to separate the effect of H_2O and O_2, and the results are also presented in Fig. 6A. The carbon loading results from adsorption under 1.5 vol.% H_2O and 10 vol.% O_2 show an insignificant change to results obtained under simulated idle exhaust gas environment, and adsorption under both conditions is significantly higher than carbon loading results under the baseline gas environment. Apparently, the presence of H_2O plays an important role in the HC adsorption process. On the other hand, increasing the O_2 level from 10 vol.% to 19 vol.%, with 8% H_2O, only resulted in a small decline in carbon loading for all three HC species. The small decrease is likely due to increased oxidation rate of adsorbed HC species resulting from higher O_2 concentration on the VSCR catalyst surface. Comparing the carbon loading results from the control experiments with 1.5% H_2O and 10% O_2 to the baseline results, it can be concluded that the increased carbon loading under simulated idle conditions is primarily due to the reduction in water content from 8% to 1.5%. Although changing O_2 level from 10% to 19% did not lead to significant differences in carbon loading, completely removing O_2 (0 vol.% O_2) resulted in substantial reductions in carbon loading for dodecane and toluene of 63% and 83%, respectively. This illustrates the nature of oxidative adsorption for dodecane and toluene. In contrast, carbon loading from squalane adsorption remains relatively unchanged without the presence of O_2, in comparison to the baseline results. As previously shown in Fig. 2, the inlet concentration of squalane is much closer to its vapor pressure at 150 °C. Presumably, (capillary) condensation plays a role in squalane adsorption on the VSCR catalyst. Fig. 6B displays TPO CO_x profiles after squalane adsorption at 150 °C for ~2 h under different gas environments with various levels of H_2O and O_2. The TPO results have similar profiles other than the overall CO_x intensity, with a major peak around 250 °C and a high temperature shoulder from 300 to 400 °C.

Thermodynamically, condensation of squalane can be expected below 110 °C since its vapor pressure is below the inlet concentration of 1.7 ppm as shown in Fig. 2. Thus, as the temperature is decreased, the effect of condensation is expected to increase and the effects from competitive adsorption with water and oxidation by O_2 are expected to decrease. Fig. 7 compares the effects of H_2O and O_2 on the carbon loading from ~2 h squalane adsorption at 80 °C and 150 °C. At 80 °C, the effect of varying H_2O and O_2 concentration is even smaller in comparison to the effect at 150 °C. For example, squalane adsorption under simulated idle exhaust conditions at 80 °C increased only 25%, much less than the 46% increase at 150 °C.

Table 3
BET surface area of HC adsorbed catalysts.

Sample	BET surface area [m^2/g]
DG VSCR	31
450 ppm dodecane 150 °C ~2 h	28
270 ppm toluene 150 °C ~2 h	30
1.7 ppm squalane 100 °C ~2 h	21
1.7 ppm squalane 150 °C ~2 h	26
1.7 ppm squalane 100 °C/225 °C cycles	26

3.5. Characterization of VSCR catalysts after HC adsorption

Due to low HC adsorption, higher concentrations of dodecane and toluene were used to prepare catalyst samples for characterization to increase signal resolution. The measured BET surface area listed in Table 3 shows that the DG VSCR has a surface area of 31 m^2/g. The adsorption of diesel model molecules, dodecane and toluene, results in only a minimal decrease in surface area in comparison to the DG VSCR. In contrast, constant temperature squalane adsorption at 100 and 150 °C and adsorption during the 100/225 °C cycling experiment results in an apparent decrease in surface area of 16 ~ 32%. The reduction in surface area can be attributed to the blockage of catalyst pores resulting from the high HC loading after squalane adsorption.

The DRIFTS spectra of DG and HC adsorbed VSCR catalysts are displayed in Fig. 8. The broad band from 2600 to 3750 cm^{-1} is attributed to the H-bonded hydroxyl groups at the catalyst surface and adsorbed water. A strong water bend mode appears at 1630 cm^{-1} on the DG VSCR. The HC adsorbed VSCR catalysts have new IR absorption features in the regions of 1550–1850 cm^{-1} and 2800–3000 cm^{-1} in comparison to the DG VSCR. Dodecane adsorption with 450 ppm at 150 °C shows broadened IR absorption features on both sides of the water bend mode at 1630 cm^{-1} (Fig. 8b). The vibration modes at 1780 and 1720 cm^{-1} can be assigned to carbonyl C=O vibration from aldehydes/ketones/carboxylic acids [12,34]. The shoulder at 1580 cm^{-1} can be ascribed to the asymmetric stretch of carboxylate anions, whose corresponding symmetric stretch at 1405 cm^{-1} is very weak but still discernable in comparison to the spectra of DG VSCR [35,36]. Some very weak C—H vibration from 2800 to 3000 cm^{-1} is also present. Dodecane adsorbed at a lower temperature of 100 °C and lower concentration, but longer duration of 6 h (Fig. 8d) displays decreased C=O carbonyl vibrations at 1780 and 1720 cm^{-1} but enhanced carboxylate anion stretches at 1580 and 1405 cm^{-1} in comparison to dodecane adsorbed at 150 °C for 2 h (Fig. 8b). The C—H vibration strength from 2800 to 3000 cm^{-1} is also enhanced. The toluene adsorbed VSCR catalyst has no apparent new IR absorption features as shown in Fig. 8c in comparison to the DG VSCR, likely due to its low adsorption amount. The squalane adsorbed VSCR catalysts display similar IR absorption bands to dodecane adsorbed VSCR catalysts with carbonyl vibrations at 1780 and 1720 cm^{-1}, carboxylate anion vibrations at 1580 and 1405 cm^{-1} and C—H vibrations from 2800 to 3000 cm^{-1}.

4. Discussion

VSCR adsorption of propylene, a light HC derived from partially combusted diesel fuel, has previously been studied by Ottinger et al. The authors found that the amount of propylene adsorption on VSCR is negligible at 150 °C [8]. Dodecane and toluene are frequently found in diesel exhaust, and they are generally thought to result from unburned diesel fuel [13,14,16,17]. In addition, they are extensively used as diesel model molecules for evaluating diesel aftertreatment catalysts [8,9,31,38,39]. The adsorption of dodecane and toluene on the VSCR catalyst from 80 to 250 °C from 2 to 12 h is illustrated in Fig. 4A and B. Condensation of dodecane and toluene

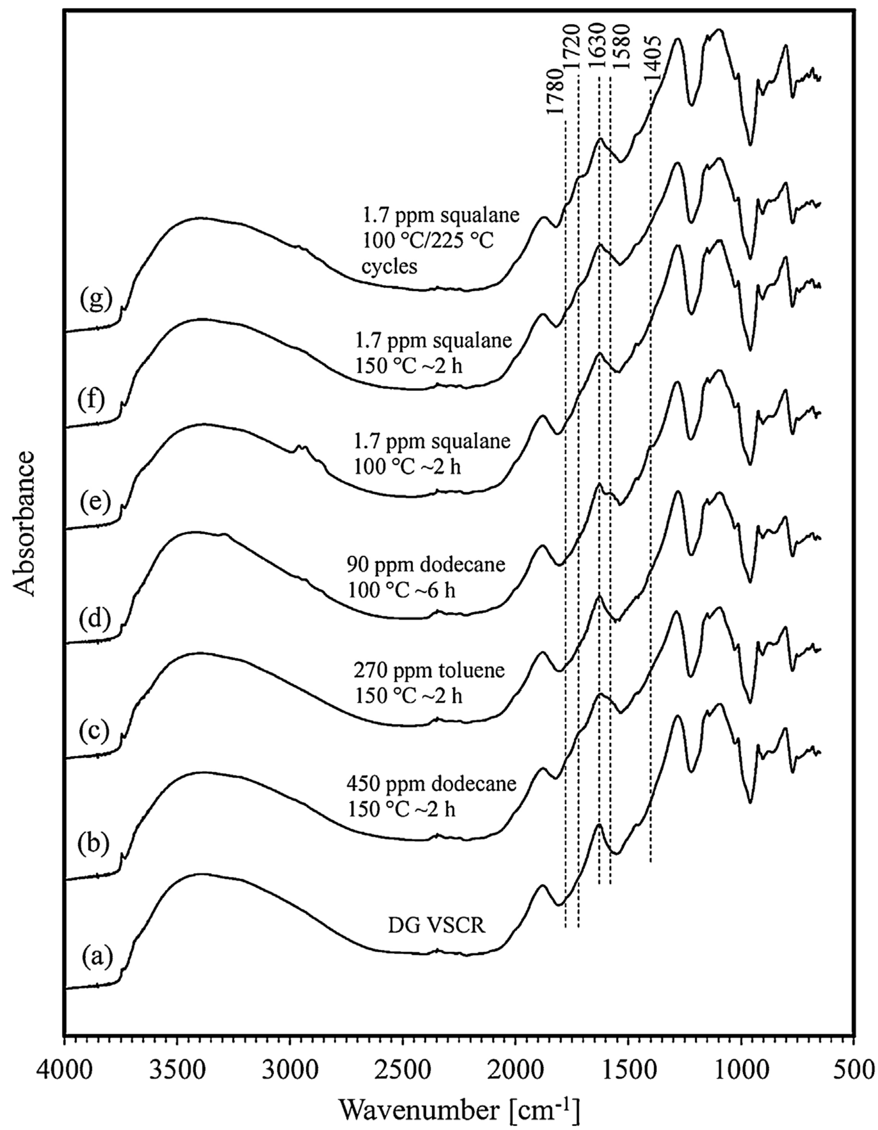


Fig. 8. DRIFTS spectra from HC adsorbed VSCR catalyst samples: (a) DG VSCR; (b) 450 ppm dodecane 150 °C ~2 h; (c) 270 ppm toluene 150 °C ~2 h; (d) 90 ppm dodecane 100 °C ~6 h; (e) 1.7 ppm squalane 100 °C ~2 h; (f) 1.7 ppm squalane 150 °C ~2 h; (g) 1.7 ppm squalane 100 °C/225 °C cycles.

can be excluded under the tested temperature range because the inlet concentration is several orders of magnitude lower than its corresponding saturation vapor pressure shown in Fig. 2. Upon exposing the VSCR catalyst to HC molecules under lean conditions, HC can be adsorbed or (partially) oxidized on the VSCR catalyst surface. The adsorbed HC species can desorb from the catalyst surface or be further oxidized. After approximately 2 h of adsorption, the carbon loading from both dodecane and toluene adsorption plateaus, indicating the adsorption/desorption/oxidation process approaches equilibrium within 2 h. Toluene adsorption on VSCR for less than 2 h was conducted at 200 °C and the results are shown in Fig. 4B. At 12 min, the toluene uptake has already reached 50% of the 2 h loading. The dodecane and toluene adsorption also display an apparent activation process. For example, the carbon loading from dodecane adsorption increases from 16 mmol/L at 80 °C to 95 mmol/L at 125 °C before decreasing to 68 mmol/L at 175 °C. With increasing adsorption temperature, the reaction rate of HC adsorption, desorption and oxidation of adsorbed HC can be expected to increase. When the HC adsorption rate exceeds the overall reaction rate of desorption and oxidation, then the carbon loading increases or vice versa. Both O_2 and H_2O play important and different roles, affecting dodecane and toluene adsorption. We did not observe apparent new IR absorption features from toluene adsorbed VSCR catalyst in comparison to the DG VSCR due to the lower uptake; however, it has been extensively reported that toluene (partial)-oxidation over V_2O_5/TiO_2 catalyst systems can form benzaldehyde and benzoic acid [37,40,41]. Besselmann et al. reported that oxidative adsorption of toluene occurs over monomeric vanadyl species of a V_2O_5/TiO_2 catalyst while no molecular adsorption of toluene is observed at 150 °C [12]. In the case of dodecane adsorption on the VSCR catalyst, new IR absorption features due to carbonyls and carboxylic anions were observed as shown in Fig. 8. These results clearly indicate that the partial oxidation of dodecane occurs during the adsorption process. Without the presence of O_2, the amount of carbon loading from dodecane and toluene adsorption significantly decreases as shown in Fig. 6A. The small amount of carbon loading measured in the absence of O_2 is likely due to partial HC oxidation by lattice oxygen associated with catalyst surface vanadia species [42]. Increasing the O_2 concentration from 10% to 19% in the presence of 8% H_2O does not result in apparent changes in carbon loading from dodecane and toluene adsorption. This result is supported by the observations of Watling et al. that propylene,

n-decane and toluene oxidation over a VSCR catalyst is zero order with respect to O_2 in the presence of 7% H_2O [9]. As previously discussed, the observed substantial increase in carbon loading from dodecane and toluene adsorption under a simulated idle exhaust environment in comparison to the base gas environment is primarily attributed to the decrease in H_2O concentration from 8% to 1.5%. It is known that H_2O can inhibit the oxidation activity of a VSCR catalyst due to the competitive adsorption of H_2O with reactants, forming hydrogen bonded or moisture solvated VOx surface species [43]. Therefore, dodecane and toluene adsorption on the VSCR catalyst appears to occur via oxidative adsorption, and the increase in carbon loading during idle conditions can be attributed to the increased oxidation reactivity of vanadia species due to decreased competitive adsorption from H_2O under lower water concentration.

Lube oil is primarily composed of a complex mixture of heavy HC from C14-C45 [21]. Squalane ($C_{30}H_{62}$), due to its physical and chemical similarity to lube oil, has been used as a model molecule for studying the degradation of lubricant due to thermo-oxidation [30] and thermal stability in the presence of sulphuric acid [44]. In contrast to dodecane and toluene, the carbon loading from squalane adsorption on VSCR increases with increasing adsorption duration as shown in Fig. 4. As was mentioned previously, the engine out exhaust concentration of lube oil derived HC is estimated to be approximately 50 ppm C1. The squalane adsorption at 150 °C is much less affected by the level of O_2 as shown in Fig. 6A. On the other hand, H_2O affects the adsorption of squalane, albeit to a lesser degree than it affects dodecane and toluene adsorption. As illustrated in Fig. 2, the inlet concentration of squalane is much closer to its vapor pressure in comparison to dodecane and toluene at temperatures below 150 °C. Commercial VSCR catalysts have a wide pore size distribution from 50 to 1000 Å [28]. It can be estimated that the vapor pressure will decrease more than 60% when the catalyst pore diameter is below 100 Å. Therefore, (capillary) condensation is likely to play a role in squalane adsorption on the VSCR catalyst at 150 °C. Reducing the adsorption temperature to 80 °C, the effects of O_2 and H_2O become even less pronounced on squalane adsorption as shown in Fig. 7. The reduced BET surface area of the squalane adsorbed VSCR catalysts in Table 3 also provides evidence of squalane condensation. Although O_2 has a much smaller impact on squalane adsorption, the adsorbed squalane gradually experiences (partial) oxidation due to its long residence time on the catalyst surface once it is condensed. Carbonyl vibrations at 1720 and 1780 cm^{-1} and carboxylate vibration at 1580 cm^{-1} can be observed on squalane adsorbed VSCR catalysts at 100 and 150 °C in Fig. 8. Thus, squalane adsorption on VSCR catalysts at low temperature is proposed to occur mainly via (capillary) condensation with subsequent oxidation over VSCR catalysts.

The TPO profiles of dodecane, toluene and squalane adsorbed VSCR catalysts all display two overlapping CO_x peaks, one major peak from 200 to 300 °C and a smaller peak from 300 to 400 °C. The two CO_x peaks likely correspond to two different types of carbonaceous materials, one with higher loading and more reactive and the other with lower loading and more stable. The underlying nature of the two different types of carbonaceous material is currently unknown. The smaller, high temperature peak may result from more strongly adsorbed organic species or more stable carbonaceous species with smaller H/C ratio, formed as a result of coking [45]. As can be seen from Fig. 5, the majority of the low temperature peak is easily removed by exposure to 225 °C, while the high temperature CO_x peak is not significantly reduced. In addition, the high temperature CO_x peak tends to move to higher temperature, indicating the adsorbed carbonaceous species become more stable upon exposure to higher temperature. Therefore, under actual diesel engine aftertreatment operating conditions, the more stable carbonaceous species are more likely to accumulate under idle and low load operating conditions. These accumulated carbonaceous species can physically block catalyst pores/sites leading to catalyst deactivation [8,37]. We did not observe apparent exotherms during TPO experiments because heat of oxidation can be effectively dissipated from the small catalyst sample. However, the heat of oxidation of carbonaceous species accumulated on a VSCR catalyst during engine operation cannot be ignored. For example, sudden increases in engine load during transient operation would likely result in rapid increases in exhaust temperature. This could lead to a rapid burn-off of accumulated carbonaceous species, generating significant exotherms across the aftertreatment system which could thermally damage aftertreatment catalysts [28,46] and lead to undesired vanadium and tungsten metal release [2]. The magnitude of the exotherm will depend on the amount of accumulated carbonaceous species and their reactivity in addition to the engine operating conditions such as exhaust flow rate, temperature ramping rate etc.

5. Conclusions

Low temperature (80–200 °C) hydrocarbon adsorption of dodecane and toluene as diesel model molecules and squalane as lube oil model molecule on a state-of-the-art VSCR catalyst was investigated in the presence of 8% H_2O and 10% O_2, simulating diesel engine exhaust conditions. Dodecane and toluene adsorb on the VSCR catalyst via an activated, oxidative adsorption process. The carbon loading from adsorption of either 1000 ppm C1 of dodecane or toluene plateaus after ~2 h of adsorption with a maximum of ~100 mmol/L carbon loading. In contrast, the amount of carbon loading from squalane adsorption increases with increasing adsorption duration from 80 to 150 °C. Squalane adsorption can be 4–6 times higher than that from 1000 ppm C1 of dodecane or toluene adsorption, even though the inlet concentration of squalane is 50 ppm C1, mimicking the estimated engine out HC contribution of unburned lube oil. Squalane adsorption on the VSCR catalyst at low temperature is proposed to occur mainly via (capillary) condensation, consistent with the decrease in BET surface area of the squalane adsorbed VSCR catalysts. The observed IR absorption attributed to carbonyl and carboxylate vibrations on dodecane and squalane adsorbed VSCR catalysts indicates (partial) oxidation occurs during the hydrocarbon adsorption process. Under a simulated idle gas environment with 1.5% H_2O and 19% O_2, the carbon loading from dodecane, toluene and squalane adsorption increases 68, 136 and 46%, respectively. Control experiments indicate that the increased carbon loading is mainly a result of lower H_2O concentration under idle conditions. TPO experiments conducted on HC adsorbed VSCR catalysts illustrate that a majority of the adsorbed carbonaceous material has high reactivity and can be oxidized at temperatures between 200 and 300 °C. The remainder of the adsorbed HC species is more stable and oxidizes between 300 and 400 °C. Results from the temperature cycling experiment show that the more stable carbonaceous material from HC adsorption is more prone to accumulate over time during transient operation of diesel engines. This work illustrates that unburned lube oil based hydrocarbon is likely the main contributor to carbonaceous deposits observed on VSCR diesel aftertreatment systems operated at low load. The loading of carbonaceous species over VSCR catalyst should be optimized during engine operation to minimize its negative effect on SCR efficiency and reduce the risk of catalyst thermal damage as well as vanadium and tungsten release.

Acknowledgements

The authors would like to acknowledge Dr. David A. Nickel, Mr. Mike A. Robinson and Dr. Christopher J. Keturakis from Cummins

Inc. for their invaluable technical discussion. The authors would also like to acknowledge Dr. Frances E. Lockwood from Valvoline for her suggestion on using squalane as a model molecule for lube oil in this study. The authors are grateful to Dr. Haomiao Zhang from Massachusetts Institute of Technology for some of the lab work when he was a co-op at Cummins Inc.

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